



TITLE:

# <Division of Synthetic Chemistry>Structural Organic Chemistry

AUTHOR(S):

---

CITATION:

<Division of Synthetic Chemistry>Structural Organic Chemistry. ICR Annual Report 2011, 18: 6-7

ISSUE DATE:

2011

URL:

<http://hdl.handle.net/2433/154972>

RIGHT:

# Division of Synthetic Chemistry – Structural Organic Chemistry –

<http://www.scl.kyoto-u.ac.jp/~kouzou/index.html>



Prof  
MURATA, Yasujiro  
(D Eng)



Assoc Prof  
WAKAMIYA, Atsushi  
(D Eng)



Assist Prof  
MURATA, Michihisa  
(D Eng)



PD  
TANIGUCHI, Takuhiro  
(D Sc)



PD  
YOSHIKAWA, Osamu  
(D Eng)



Res  
ENDOU, Masaru

## Researcher

NISHIDA, Tomoko

## Students

MORINAKA, Yuta (D2)

KATSUYA, Satoshi (M2)

NOBORI, Masahiro (M2)

NISHIMURA, Hidetaka (M1)

MORI, Haruki (M1)

ZHANG, Rui (RS)

SAKURAI, Yuko (UG)

SHIMOGAWA, Hiroyuki (UG)

## Visitors

Prof DENNIS, John

Prof WÜRTHEIN, Ernst-Ulrich

Prof MARGETIĆ, Davor

School of Physics, Queen Mary, University of London, U.K., 18 April

Organisch-Chemisches Institut, Westfälische Wilhelms-Universität, Germany, 8 October

Division of Organic Chemistry and Biochemistry, Ruđer Bošković Institute, Croatia,  
7 December

Prof LIU, Shih-Yuan

Prof WU, Jishan

Department of Chemistry, University of Oregon, U.S.A., 12 December

Department of Chemistry, National University of Singapore, Singapore, 22 December

## Scope of Research

Fundamental studies are being conducted for creation of new functional  $\pi$ -systems with novel structures and properties, and for evaluation of their application as organic semi-conducting materials toward photovoltaic and electroluminescent devices. The major subjects are: organo-chemical transformation of fullerenes  $C_{60}$  and  $C_{70}$ , specifically organic synthesis of endohedral fullerenes by the technique of molecular surgery; generation of ionic fullerene species and their application for the synthesis of functional material; synthesis of new carbon-rich materials by the use of transition metal complex; creation of new functional  $\pi$ -materials with unique photoelectric properties.

## Selected Publications

Morinaka, Y.; Tanabe, F.; Murata, M.; Murata, Y.; Komatsu, K., Rational Synthesis, Enrichment, and  $^{13}C$  NMR Spectra of Endohedral  $C_{60}$  and  $C_{70}$  Encapsulating a Helium Atom, *Chem. Commun.*, **46**, 4532-4534 (2010).

Job, A.; Wakamiya, A.; Kehr, G.; Erker, G.; Yamaguchi, S., Electronic Tuning of Thiazolyl-Capped  $\pi$ -Conjugated Compounds via a Coordination/Cyclization Protocol with  $B(C_6F_5)_3$ , *Org. Lett.*, **12**, 5470-5473 (2010).

Murata, M.; Morinaka, Y.; Murata, Y.; Yoshikawa, O.; Sagawa, T.; Yoshikawa, S., Modification of  $\sigma$ -Framework of [60]Fullerene for Bulk-heterojunction Solar Cells, *Chem. Commun.*, **47**, 7335-7337 (2011).

Frunzi, M.; Jockusch, S.; Chen, J. Y. -C.; Calderon, R. K.; Lei, X.; Murata, Y.; Komatsu, K.; Guldi, D. M.; Lawler, R. G.; Turro, N. J., A Photochemical On-Off Switch for Tuning the Equilibrium Mixture of  $H_2$  Nuclear Spin Isomers as a Function of Temperature, *J. Am. Chem. Soc.*, **133**, 14232-14235 (2011).

Kurotobi, K.; Murata, Y., A Single Molecule of Water Encapsulated in Fullerene  $C_{60}$ , *Science*, **333**, 613-616 (2011).



## KEYWORDS

$\pi$ -Conjugated Systems  
Open-Cage Fullerenes  
Endohedral Fullerenes

Functional Dyes  
Organic Solar Cell

## A Single Molecule of Water Encapsulated in Fullerene C<sub>60</sub>

The C<sub>60</sub> encapsulating a water described here is a totally new member of endohedral fullerenes produced only by the present method. In contrast with the maturity of the science of empty fullerenes, research on endohedral fullerenes has not been fully developed in spite of their potentiality for various applications. This is ascribed to severe limitations in their production and isolation with high purity even in mg quantities. Their current production relying on physical method needs to be improved. We have succeeded in the macroscopic production of endohedral C<sub>60</sub> encapsulating a water molecule in 100%, by a new approach using the methodology of organic synthesis with the dynamic control of the opening-size on an open-cage fullerene derivative. This result indicates that currently employed physical method for the production of endohedral fullerenes, which relies on accidental and uncontrollable self-assembly of atoms, can be replaced by the fully controlled and rational synthetic method of much higher efficiency.

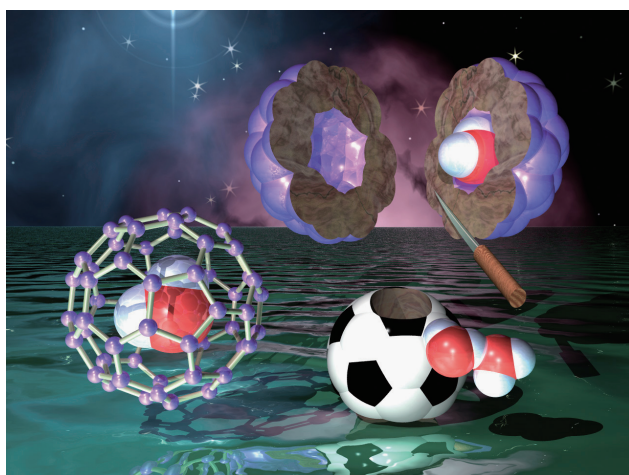


Figure 1. Molecular structure of H<sub>2</sub>O@C<sub>60</sub>.

## Modification of $\sigma$ -Framework of C<sub>60</sub> for Bulk-heterojunction Solar Cells

The organic thin-film photovoltaic devices, so called bulk-heterojunction (BHJ) solar cell, possesses a high potentiality as a renewable energy source because of its easy fabrication through solution process, flexibility, and large area application. In the BHJ cells [60]Fullerene derivatives have occupied a dominant position as an n-type organic semiconductor. However, much effort has so far been focused on developments of the donor polymer, while those of n-type materials remain untapped although some simple addition reactions to the surface of the C<sub>60</sub> cage are used. In this study, we have clearly demonstrated that the skeletal-modification of C<sub>60</sub> can be used to control the electronic properties and, thus, can be a promising avenue toward the novel acceptor materials for the BHJ solar cells. The device using the skeletally-modified C<sub>60</sub> derivative marked excellent open-circuit voltage ( $V_{oc}$ =0.74 V) and power conversion efficiency

( $\eta_e$ =3.1%) with reference to the device using the benchmark acceptor PCBM ( $V_{oc}$ =0.60 V,  $\eta_e$ =3.1%).

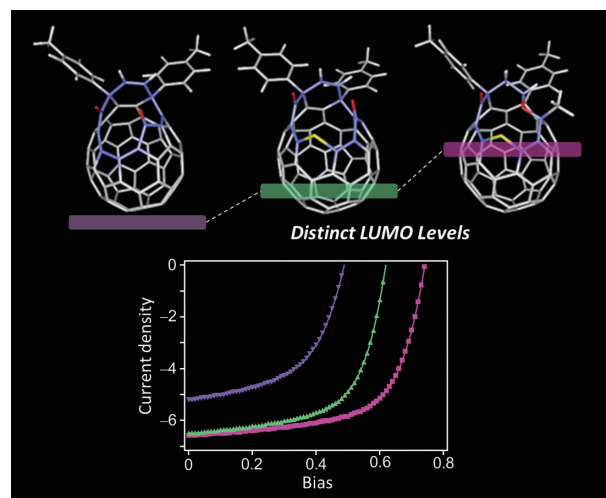


Figure 2. Open-cage C<sub>60</sub> derivatives and their application to the bulk-heterojunction solar cells.

## Planarized Triaryboranes as Boron-embedded 2D $\pi$ Scaffolds

Electron-accepting  $\pi$ -conjugated skeletons have long been sought for development of excellent n-type semiconducting materials in organic electronics. Incorporation of electron-deficient boron atoms into a two-dimensionally expanded  $\pi$ -skeleton should be a promising strategy to this end. As a simple example, we now synthesize triphenylborane and its diboron homologue that are completely planarized with methylene tethers. In contrast to the conventional concept for the kinetic stabilization of boron-containing materials by bulky substituents, the produced compounds show high stability toward air and moisture, and even toward Lewis acidic amines despite the absence of steric protection around the boron moiety. These results should give a new paradigm for the stabilization of the tri-coordinate boron-containing materials. A notable advantage to embed the boron atoms into the  $\pi$ -skeleton is to allow us the structural and properties modification based on the coordination number change of the boron atoms. Indeed, upon treatment with fluoride ions, the triphenylborane derivatives undergo the plane-to-bowl conversion in a controlled manner.

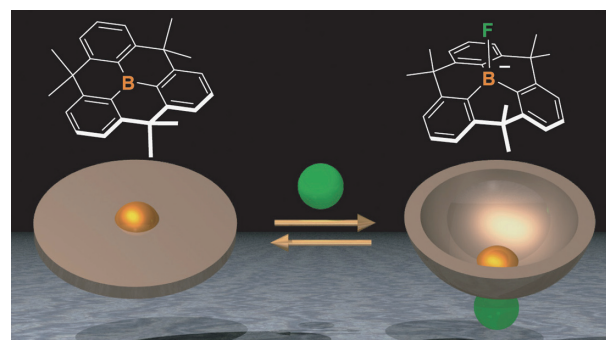


Figure 3. A controlled plane-to-bowl conversion based on the coordination number change of the boron atom.